SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT N" : BREU-CT91-0424 (DTEE)

PROJECT N" : P-4215
BE

TITLE: **Improved Tyre Safety and Life by a New Wire/Rubber Adhesion System**

PROJECT CO-ORDINATOR: Pirel i Coordinamento Pneumatic Spa.

PARTNERS : University of Nottingham
Rhone-Poulenc Chimie SA
Instituto Nazionale per la Fisica dells Materia

STARTING DATE : 1/6/91 DURATION :48 MONTHS

PROJECT FUNDED BY THE EUROPEAN COMMUNITY UNDER THE BRITE/EURAM PROGRAMME

1. Titles, Authors names and addresses

PROJECT: BREU-0424.

TITLE: Improved Tyre Safety and Life by a New Wire/Rubber Adhesion System

Dr G. Orjela (Project Coordinator)
Pirelli Coordinamento Pneumatic
Vaile Sarca 222
20126 Milano
Italia
Tel. +39-2-6442-33 13

Prof S. J. Harris
Department of Material Engineering& Design
University of Nottingham
University Park
Nottingham NG72RD, UK
Tel. +44-1 15-951-3741

Ms. M. Vincent
Rhone Poulenc Chimie
Centre de Recherches d'Aubervilliers
52, rue de la Haie-Coq
93308 Aubervilliers Cedex
France
Tel. +33-1-47681953

Prof. F. Tommasini
Laboratorio TASC, Consorzio INFM
Padriciano, 99
34012 Trieste
Italia
Tel. +39-40-3756420

2. **Abstract**

A new wire/rubber adhesion system based on an innovative new coating has been researched and developed to the pre-competitive situation in this project. The superior performance of the system has been verified in prototype tyres. The work has substantially improved our scientific and technical knowledge of plating and tribological behaviour of zinc and zinc based alloys as well as their adhesion mechanism with natural rubber based compounds.

Traditionally, a coating of brass (30-40 wt ‰ copper) is extensively used as an adhesive to bond steel cord and natural rubber based compounds in tyres. The coating is applied electrochemically during the steel cord production process prior to fine filament drawing in a lubricant bath from typically 1.4 rnm filament to 0.2 mm filament. The brass besides being an adhesive acts as a lubricant during the drawing process. Later the filaments are formed into cords and incorporated in tyres as reinforcements. The wire/rubber bond is formed during the vulcanisation process of the tyres. This brass/rubber system however has the following deficiencies a) at low and neutral pH, the brass is cathodic to steel and thus accelerates the corrosion of the steel wire, b) at high pH the brass itself corrodes through dezincification followed by dissolution. and c) the brass/rubber bond is susceptible to attack by amine compounds.

The co-ordinator, Pirelli, of this project had developed a new wire/rubber adhesion system for use in tyres or other rubber goods which overcame these deficiencies. The new system was based on a new innovative coating composed of an inner core layer of ZnCo and an outer layer of NiZn.

The system, although showing superior wire/rubber adhesion performance, could not be drawn in commercial manufacturing conditions. Pirelli with its core competencies in steel cord manufacturing and wire rubber adhesion needed help from experts in the field of tribology/lubricants (Rhone Poulenc), plating and corrosion (Nottingham University), surface and interface analysis (INFM TASC). This consortium through a scientific approach showed:

- In the dual layer coating; the NiZn (which is difficult to draw) tends to flow into the ZnCo inner layer coating or "wear off' during the drawing process.
- Nickel does not participate in the wire/rubber adhesion bond contrary to the state-of-the-art and therefore is not necessary for wire/rubber adhesion. A single layer of ZnCo is sufficient.
- Cobalt in the ZnCo coating is concentrated at the iron interface and imparts a better corrosion performance than pure zinc.
- Drawability of the ZnCo can be obtained by reducing the thermal heating of the wire during drawing by: a) using a plating morphology with mixed crystal orientation, b) avoiding tungsten carbide dies in the last drawing passes (eliminating welding), c) using thermally stable lubricants.

Based on this information; scientific theories were developed and the coating modified so as to give the drawing performances required, while maintaing the corrosion and wire/rubber adhesion performances of the new wire/rubber adhesion system.

The consortium demonstrated that the new modified coating can be drawn in industrial conditions with less energy usage (approx. 80%) and lower costs (approx. 70%) than the brass benchmark.

Prototype passenger tyres were built with this new adhesion system. They were then tested in indoor laboratory tests and outdoor automobile field tests up to 110,000 km. In this direct comparison with the traditional brass system, the prototypes showed equal adhesion performance with superior corrosion resistance. This verification implies that the safety and life of tyres has been improved. Pirelli is currently running a program in which the system is applied to truck tyres where the benefits will have more commercial value.

4. Technical Description

The project was highly interdisciplinary and required many scientific and technical discussions to interpret the results. These interpretations were then verified with new studies and hypothesis formed. Each partner worked on their core scientific and technical competence although much interchange did occur.

The scientific and technical description can be summarised in two parts:

Part 1: Feasibility of drawing and verification of drawing in the pilot plant
Part 2: Building and testing of prototypes.

Part 1 was found to be much more difficult than envisaged at the start of the project; in fact work required for a successful mid term assessment was not concluded until October 1993 instead of January 1993. Part 2 was carried out on passenger tyre prototypes in order to reduce risk (the adhesion system was very much different to the one initially defined) while maintaining the objectives of the project.

The major **highlights for part 1 areas** follows:

a) Physical/Chemical models were agreed and constructed together by the partners for both the drawing and adhesion processes based on the prior art know-how. These models helped transfer the technology gained by Pirelli prior to the start of the project to the other partners. They also served as a basis of future work. As new results were obtained during the, work the models were updated to take account of this information. A comparison of the initial models and the final model demonstrate the major scientific and technical advances made as a result of this project. The original adhesion model was more significantly changed than the initial drawing model.

b) Laboratory tribology studies using predictive tests are not sufficiently sensitive to discriminate between lubricants. This is probably due to:
- differences in the plating used in the laboratory specimens and those used in industrial conditions
- differences in drawing mechanism

Details are given in annex 3. Attempts to improve the predictability of laboratory equipment were not successful hence all drawing development work was carried out in the Pirelli pilot plant

c) Laboratory plating studies were sufficient to develop efficient plating processes, coating chemistries and morphologies. The information obtained from these basic studies was later transferred to the pilot plant plating. The up-scaling to the pilot plant confirmed the effects of plating parameters on coating characteristics as found in the laboratory.

d) It was confirmed that the dual layer coating from background work cannot be drawn in industrial conditions:

Coating	Total Thickness	Drawing Performance km before die wear
S2 or PP5	2pm	100
Reference Brass	2pm	2000

e) Simple coating changes could not improve the drawability:

Coating	Total Thickness	Thickness Ratio	Drawing Performance km before die wear
S2 or PP5	2pm	3:1	100
ZnCo/NiZn	4pm	1:1	0.2
ZnCo/NiZn	4pm	5:1	0.2
ZnCo/NiZn	1pm	1:1	0.2
ZnCo/NiZn	1pm	5:1	0.2
Reference Brass	2pm		2000

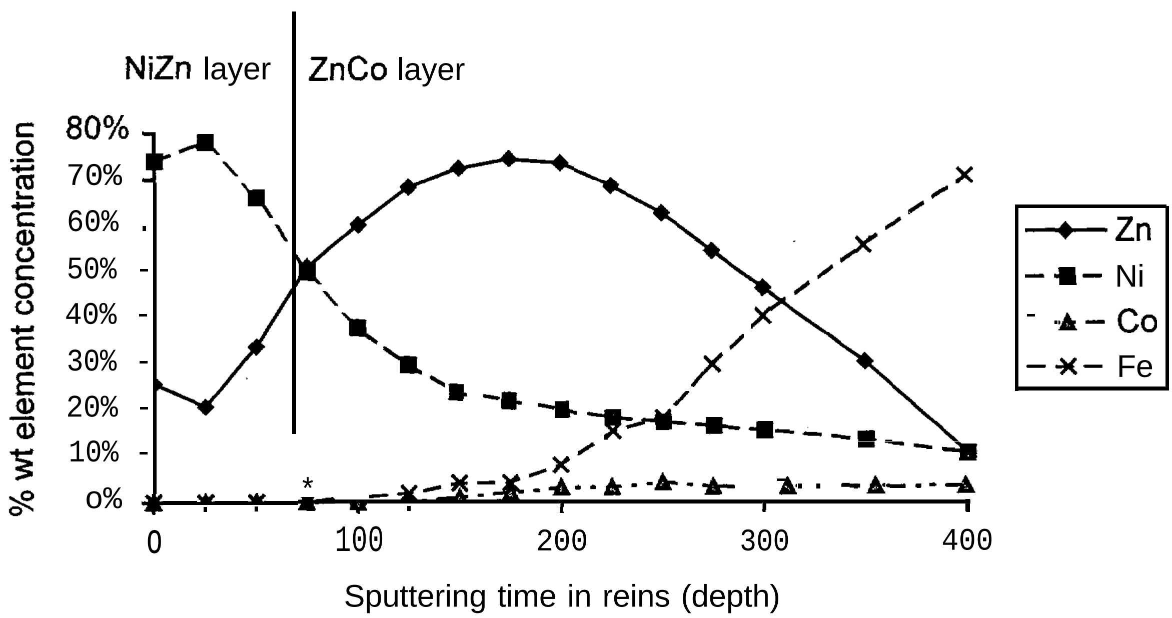
f) Known lubricant technologies were shown not to be the key to meeting the drawability objective of the project. Below are the results of pilot plant drawing using all known lubricant technologies, of the dual layer coating plated in the pilot plant

Lubricant	Technology Base	Drawing Performance km before die wear
A	Liquid dispersion	11
B	Liquid dispersion	10
C	Liquid dispersion	2
D	Wax	10
E	Solid Dispersion	6
F	Oil Base	25 (wire break)
G	Liquid dispersion	100
	Reference Brass	2000

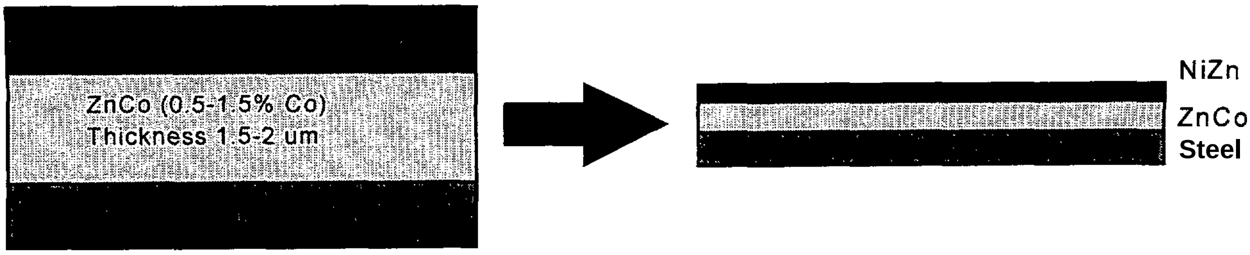
g) All potential surface analysis techniques were examined. Auger electron spectroscopy (AES) was chosen for the majority of the work mainly due to its speed of analysis without loss of information. A new sample chamber developed to overcome errors during ion gun sputtering and reduce the analysis time per specimen. Further modifications were carried out to improve the quality of the information from the instrument.

h) Surface analysis with support from scanning electron microscopy and transmission electron microscope indicated that prior art hypothesis in which the coating remained two layers after drawing is not correct. Below is shown the depth profile of the dual layer coating on steel before and after drawing.

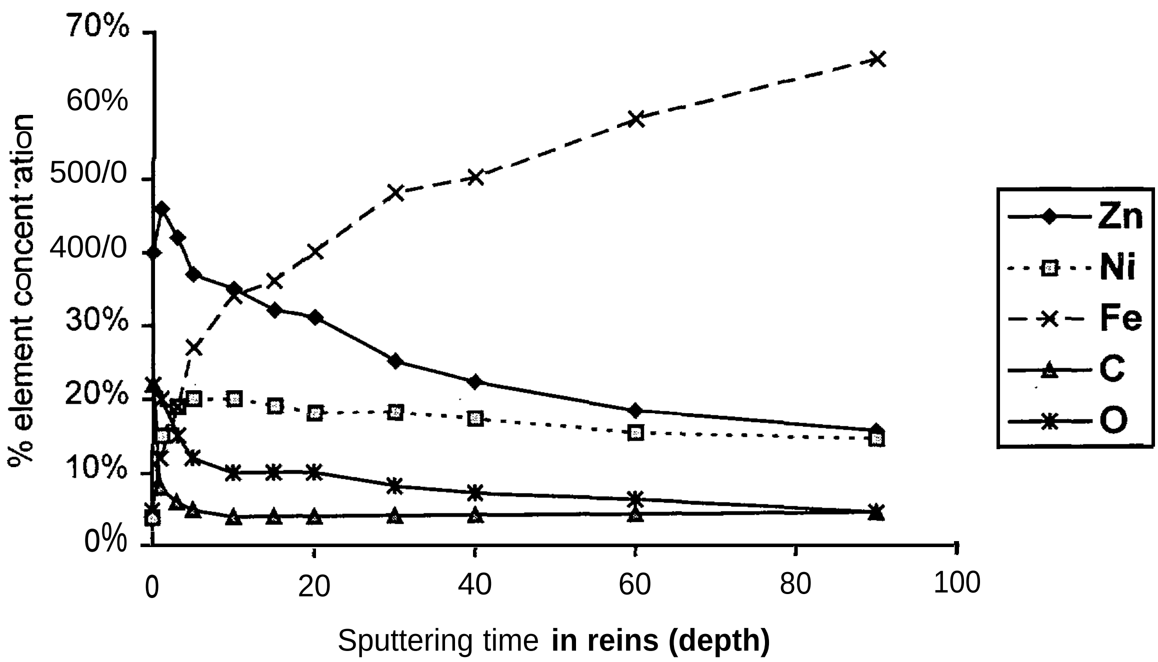
1.4 mm plated wire AES depth profile showing a two layer coating



Drawing from 1.4mm to 0.25 mm



AES of drawm **wire shows diffused lavers**



Transmission electron microscopy and x-ray diffraction confirmed that the two phases, zinc cobalt and zinc nickel remained distinct phases after drawing. However it is erroneous to conclude that these phases remained as two layers after drawing. In fact analysis by scanning auger electron spectroscopy and scanning electron microscopy analysis showed that the two phases were not in layers. It appears that some of the hard nickel phase penetrates into the softer ZnCo phase and the rest is worn away during drawing.

i) Since the above results suggested that some hypothesis of previous work may not be completely correct, a design experiment was developed. The basis of the design was to include nickel on the zinc cobalt coating in such a way that it had the least impact on drawability i.e. thinner nickel zinc coating or the use of thinner pure nickel coatings. Pure zinc cobalt in the drawable cobalt concentration range were used as a first layer. Single layers of the first coating were also considered. In addition pure nickel and nickel zinc were plated (the former being undrawable). The major premise of this work was that nickel was required for adhesion to rubber.

Below are the coatings in the designed experiment:

PP	ZnCo		90%Ni Zn	Pure Ni
Sample	Thickness	% co	Thickness	Thickness
13	1.5 urn	0		
14	1.5	0		0.1 urn
15	1.5	0		0.25
16	1.5	0		0.5
17	1.5	0	0.1 urn	
18	1.5	0	0.25	
19	1.5	0	0.5	
20	1.5	0.5 urn		
21	1.5	0.5		0.1
22	1.5	0.5		0.25
23	1.5	0.5		0.5
24	1.5	0.5	0.1	
25	1.5	0.5	0.25	
26	1.5	0.5	0.5	
27	1.5	4 urn		
28	1.5	4		0.1
29	1.5	4		0.25
30	1.5	4		0.5
31	1.5	4	0.1	
32	1.5	4	0,25	
33	1.5	4	0.5	

Adhesion studies were carried out with the prior art coating to investigate the influence of coating parameters as well as rubber compound formulation. Surface and interface studies were also carried out on all drawn samples and selected interfaces

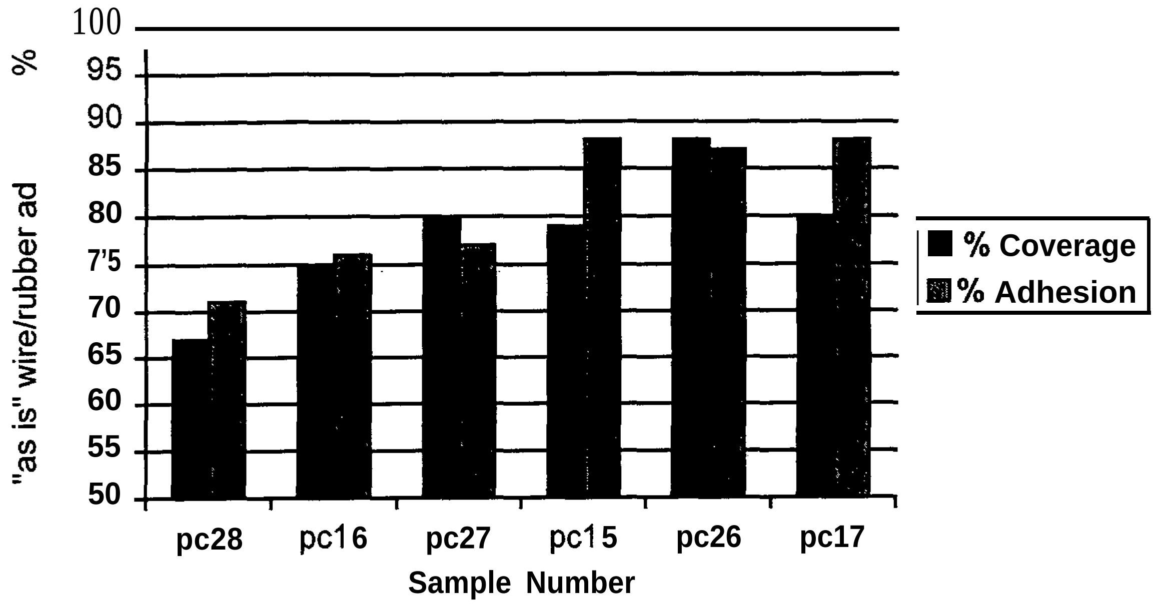
Based on these results following conclusions were made:

- T'he prior art wire/rubber adhesion theory, based on plated plates, is invalid for plated wire because pure nickel plated wire does not adhere to natural rubber compound with cobalt salt. The theory is based on the need to have nickel as a bonding agent.

In the original theory; the nickel on the outer surface of the coating reacts with the rubber to form Ni_xS_y which acts a mechanical adhesive bond with the rubber. Zinc prevents the formation of dendritic NiS (which leads to degradation of the mechanical bond) and increases the corrosion resistance of the steel core. Cobalt increases the corrosion resistance of the zinc coating.
Note that wire/rubber adhesion was found with single layer NiZn coated wire. Analysis showed no NiS; hence it was concluded that the adhesion was due to rubber reaction with zinc as in the case of ZnCo coatings.

- Cobalt salt (around a level of 1 part per hundred rubber) is necessary to adhere zinc based coatings and dual layer coatings. The adhesion mechanism therefore is related to zinc and cobalt in the compound.

- Nickel has no beneficial effect on adhesion or drawing. The results confirmed that the hard nickel goes into the soft ZnCo and wears off the coating (giving high coating weight loss during drawing) during the drawing process. This was confirmed by correlating the % Fe detected by XPS on drawn coatings (o/o coverage) and the adhesion pull out force as a % maximum adhesion force.



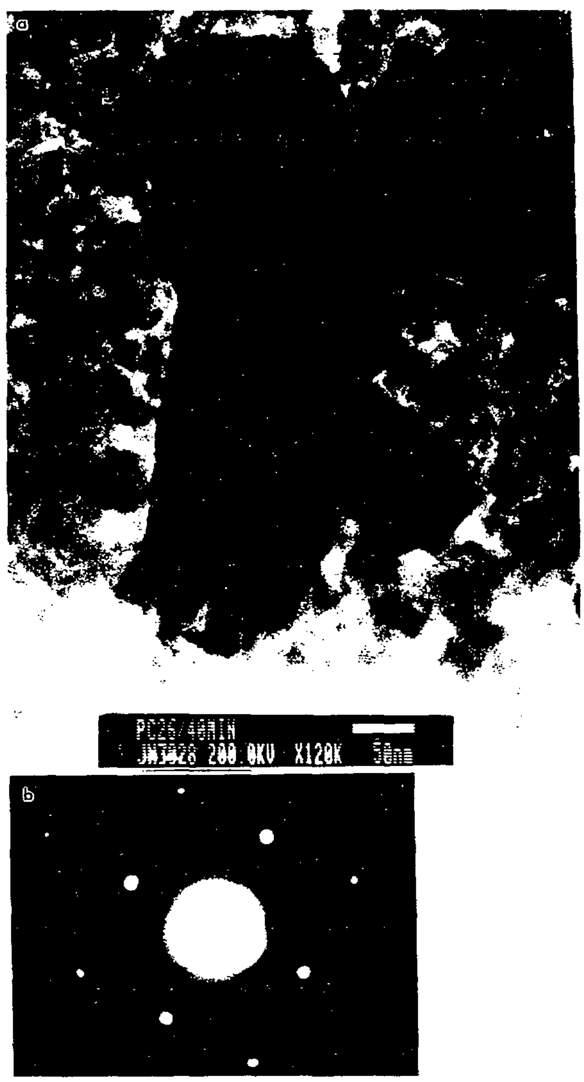


Fig. 16. (a) High magnification TEM micrograph showing the attachment of the Zn crystals to the rubber; (b) Selected area electron diffraction pattern associated with the zinc crystals.

- Zinc is element related to adhesion. In fact TEM studies of interfaces between rubber and the coating after adhesion formation show no interface products between zinc and the rubber compound. Micrographs of these findings are shown below. No NiS or ZnS was found in samples after adhesion formation.

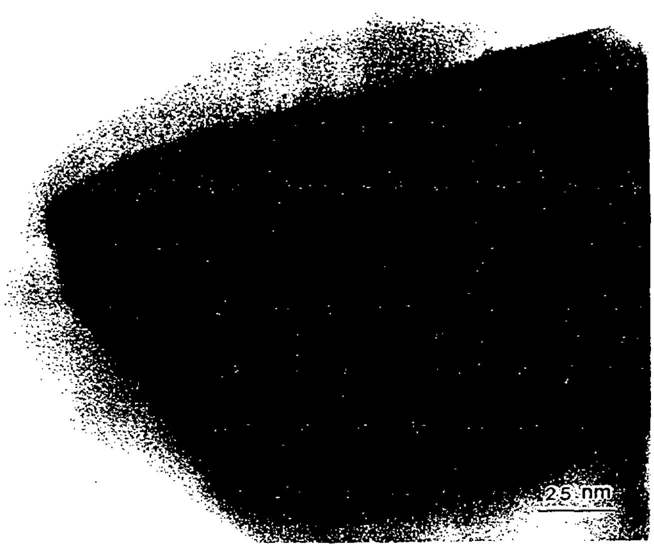
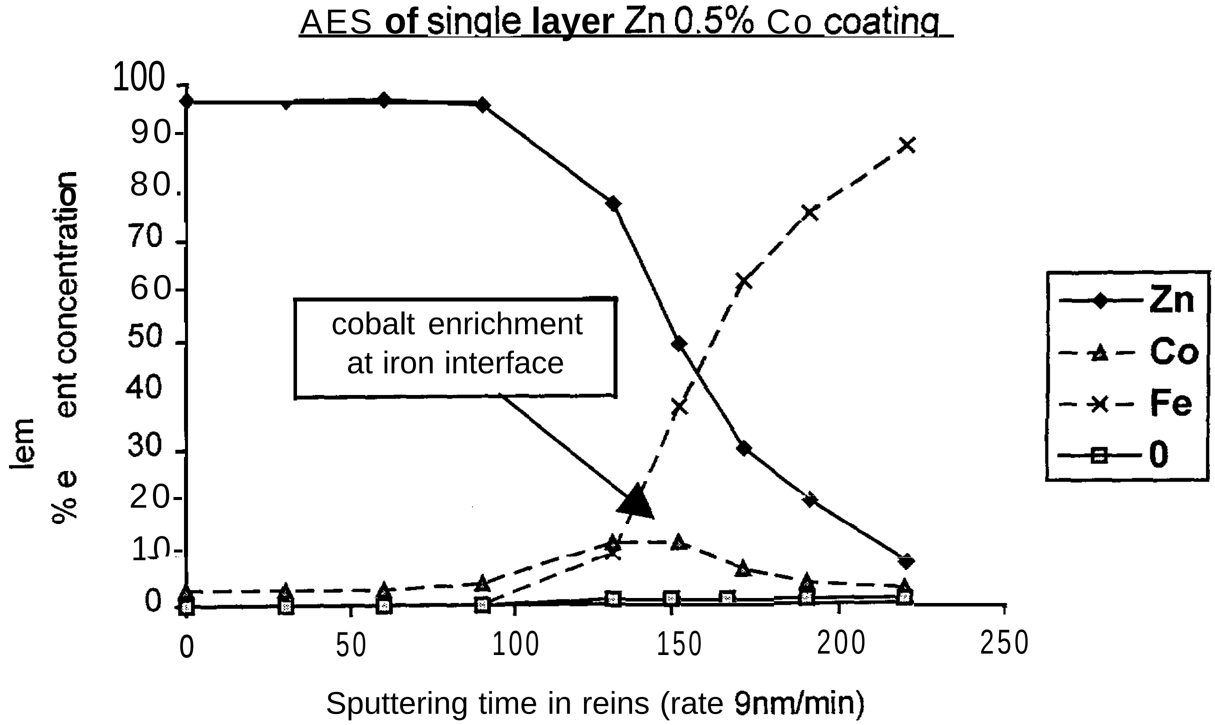


Fig. 17. Possible amorphous reaction product (thickness 20nm) associated with the zinc-rubber interface.

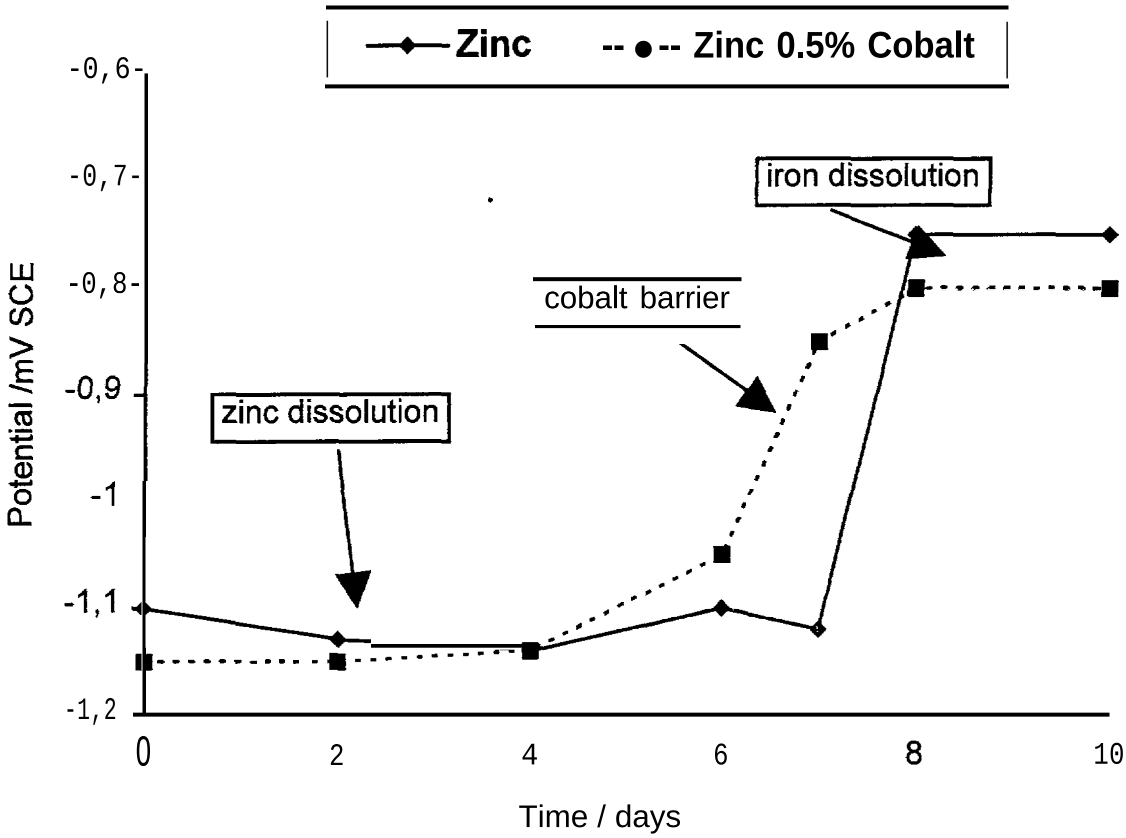
. The cobalt in the zinc cobalt was found to be enriched at the iron surface due to anomalous plating. AES analysis shown below, confirmed this enrichment.



- Corrosion studies using standard corrosion tests showed, that the zinc cobalt coating has similar corrosion resistance to the dual layer coating. The corrosion resistance is twice that of zinc and very similar to the dual layer coating as shown below.

Coating	Corrosion Resistance
Brass .	100
Zinc	2500
Zinc 0.5% Cobalt	5000
Dual Layer	5200

- Electrochemical monitoring of the electrode potential of zinc and zinc cobalt wires after drawing showed that this improved corrosion resistance is related to the barrier of cobalt enriched layer at the iron interface. In the case ‘of zinc only the electrode potential of zinc and iron are observed. In the case of zinc cobalt three electrode potential arrests are observed. The middle arrest can be assigned to the cobalt barrier. Note that this improvement in corrosion resistance is only related to thin coating in which this barrier is relatively thick.



In conclusion, the results of the designed study showed that a single zinc cobalt layer (which is more easily drawable than nickel and its alloys) gives similar wire rubber adhesion and corrosion resistance as the prior art dual layer. Thus further work was carried out on a single layer zinc cobalt coating.

h) Zinc cobalt layer was fine tuned by plating in a mixed morphology and drawing using diamond dies at the last five dies. The drawability of 0.5 tons produced in these conditions were equivalent to brass.

i) Adhesion studies and accelerated corrosion testing of tyres with the modified coating confirmed the single coating to be the optimum for continuation of the work.

In summary the results of part 1 can be presented as below:

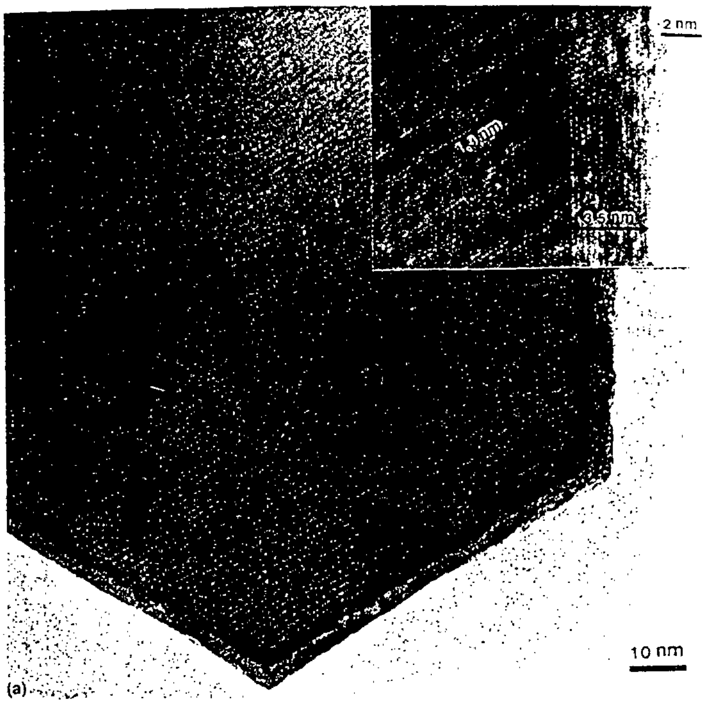
COATING	DRAWING ENERGY	ADHESION AS IS	ADHESION DEGRADATION	CORROSION RESISTANCE
Brass	100	100	100	100
Zinc 0.5%Co	≅ 80	100	100	5000
ZnCo/NiZn	100	100	50-80	5200

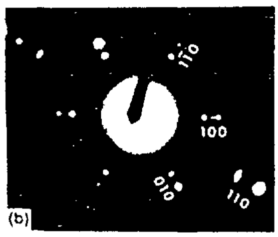
Based on these results the mid term assessment were positive and the project continued to part 2.

The following are the main **highlights of part 2:**

a) Further evidence showed that the adhesion mechanism is that of a chemical bond between zinc in the coating and sulphur in the compound.

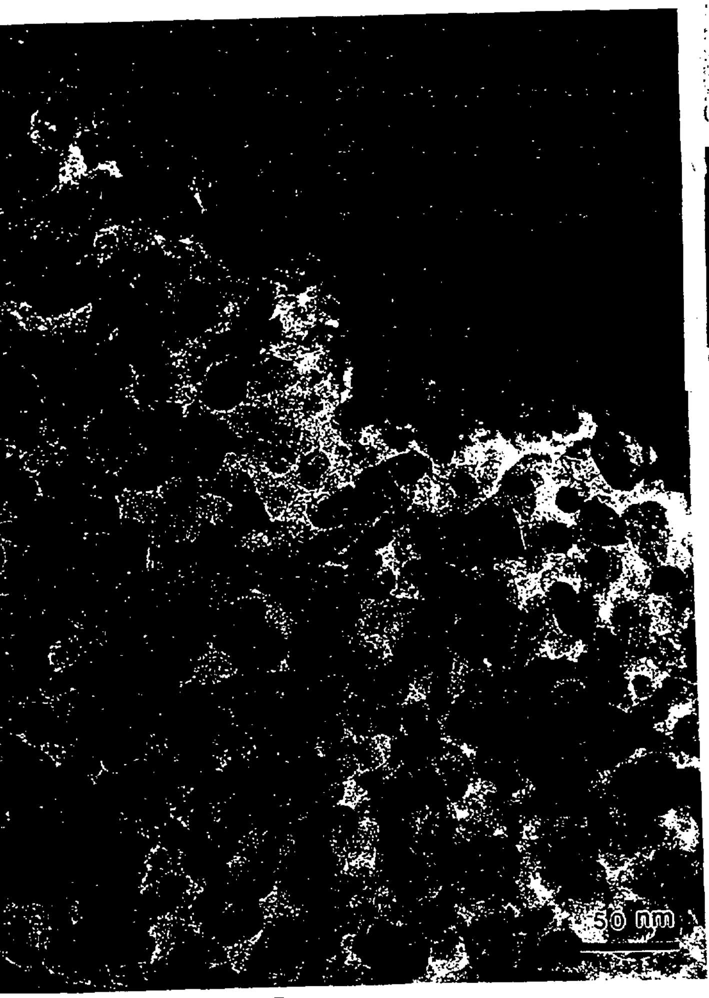
b) A cobalt salt is required in the rubber compound in order to obtain adhesion. TEM evidence shows that the ZnCo coating prior to adhesion is composed of zinc crystals covered by a zinc oxide film (see micrograph on right). After adhesion the oxide film is not present at the wire/rubber interface. It is thought that the cobalt reacts with the oxide and thus allows chemical reaction of the zinc and sulphur.





(a) A high resolution image of an individual crystallite showing the presence of moire fringes and a ZnO layer around the edge of the crystallite. The (100) lattice fringes for both Zn and ZnO are clearly seen at even high resolution.
(b) Electron diffraction pattern 01 the above crystallite, indicating the crystallite consisting of the Zn and ZnO in epitaxial alignment around the <001> orientation

c) Adhesion degradation is related to the formation of ZnS and/or ZnO. (see micrograph on left)



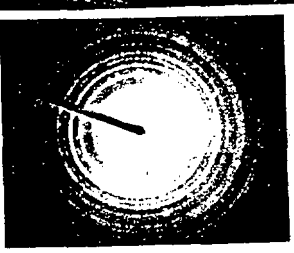


Fig. 18. TEM micrograph and selected area diffraction pattern taken from aged sample (PP13) showing evidence of interracial reaction products which were a mixture of ZnO and ZnS.

d) Further degradation can occur due to formation of zinc carbonate on the zinc coating not in contact with rubber.

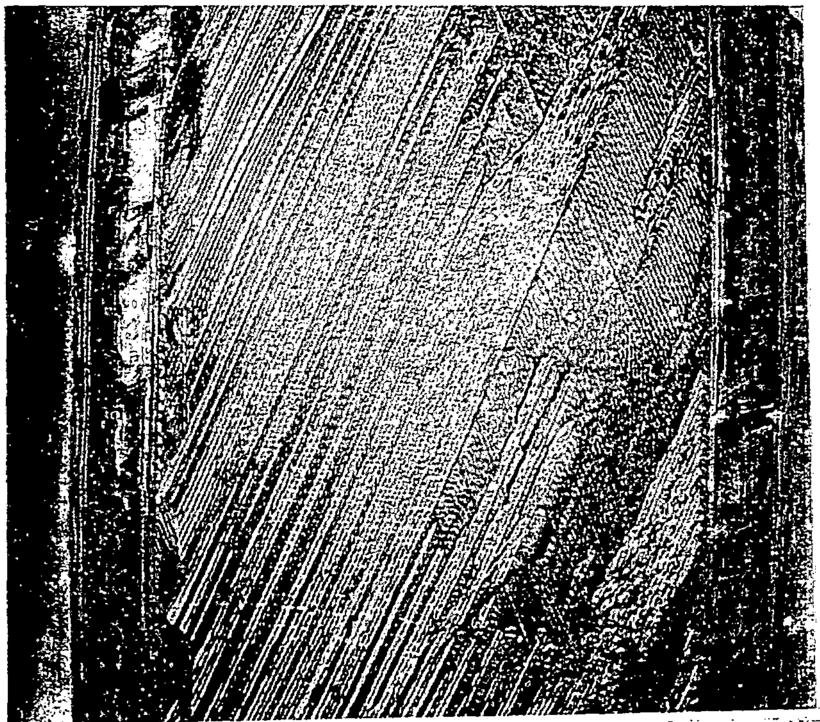
e) Tyres (195/65R14 P2000) were made with the new wire coating and the results showed:
. Equivalent indoor tyre test performance as brass benchmark:

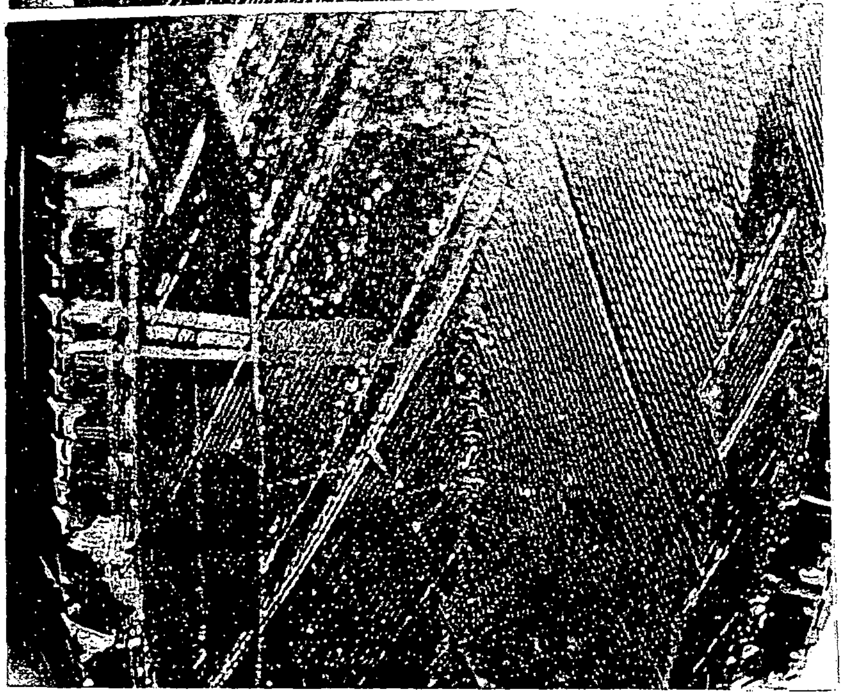
Coating	Cord	High Speed Test max. speed km/hr	Bead Fatigue Test hours before failure
Brass	2+1x0.28	260	80
ZnCo	2+1x0.28	250	72
ZnCo	3x0.28	250	92

. Equivalent 50,000 km durability on outdoor fleet testing as brass. 4 tires of each type were run on the standard route (citiblock - farm - interstate - track at speeds: as posted - 113 kph -32 kph -21 kph, respectively) at maximum load. All tyres survived this 50,000 km test.

• Equivalent 110,000 km outdoor wear tests results

• Superior corrosion resistance in Pirelli indoor tyre corrosion test. Photographs of the tyres after 200 hrs running at standard inflation and load, with the tread removed, in the Pirelli salt corrosion test are shown on the right. The top picture is the traditional coating in which,' the cords have been severely corroded, The bottom picture is that of the new coating and in which the corrosion has been contained.





The tyres after the durability and wear tests were cut to examine the belts. The examination showed that the wire/rubber adhesion was good (all cords were covered with rubber) for both the brass and ZnCo cords. However, separation in-between the two belts were present in the ZnCo tyres i.e. the compound had fatigued. Thus the compound for the new wire/rubber adhesion system needs to be fine tuned to improve its fatigue performance. Pirelli has developed compounds to overcome this performance deficiency. Details of this work are given in annex 4.

f) Laboratory adhesion cured and degraded samples in the laboratory showed similar interface products as the interface products found in tyres. This confirms the validity of Pirelli laboratory tests

g) Green aged adhesion tests show very poor performance. In fact due to the new chemistry (zinc forms non adhesive zinc carbonate film with logarithmic kinetics) the test had to modified. A lower temperature is to be used.

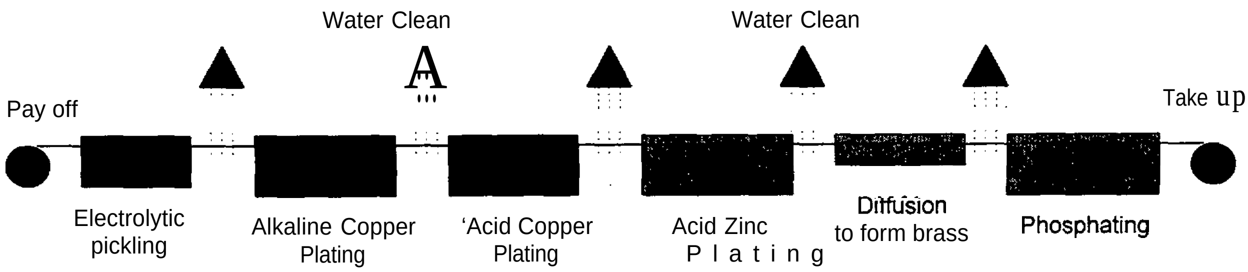
h) Rhone Poulenc developed a new lubricant based on the need to have higher thermally stable lubricating chemicals in the lubricant. This lubricant was evaluated in the pilot plant and after 0.5 tons of drawing no die wear was observed.

6. **Conclusions**

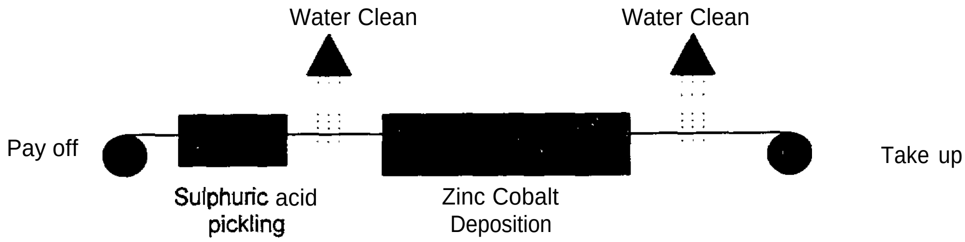
The main conclusion of the work is that a steel cord with a new advanced coating has been produced in a commercial manufacturing process. Passenger tyres, incorporating this coating, confirm that the new wire/rubber adhesion bond is at least equal to that of brass/rubber and has superior corrosion resistance to the brass benchmark.
This superior corrosion resistance reduces the possibility of adhesion loss between the steel and rubber thus improving the tyre safety and life. The tyre verification has shown that although the wire/rubber bond is at least equal to the benchmark, the rubber compound in contact with the wire needs to be modified for improved fatigue performance. These modifications have been made and Pirelli is currently running a truck tyre program to measure the improvement before further exploitation.

The new plating process uses less than 80’% energy compared to the brass benchmark and a comparison of the current and new process show a potential cost saving of 30°/0. This can easily be understood by the comparison of plating lines shown below.

A new lubricant which allows the drawing of the coating without die wear has been developed by Rhone Poulenc based on knowledge gained in this work. The lubricant performance has been verified in the Pirelli pilot plant. Rhone Poulenc is currently evaluating this lubricant on traditional brass drawing lines in order to expand its market.



Brass Plating Line Length 55m



ZnCo Plating Line Length 40m, Cost 70% Vs Brass

The work has resulted in new scientific knowledge:

Drawability

- Nickel and nickel based alloys are difficult to draw whether as pure coatings or on top of ZnCo coatings due to their hard structure. In the case of dual layer coatings ZnNi on top of ZnCo; the hard nickel phase literally gorges into the relatively soft ZnCo phase. Fortunately, the nickel is not the bases of wire rubber adhesion and therefore can be eliminated from the coating.
- Zinc cobalt on the other hand is more easily drawable. The higher the % cobalt the more difficult the drawability. The poorer drawability of zinc cobalt is related to higher heat buildup (compared to brass) during drawing which tends to reduce the lubrication efficiency. This can be overcome in part by orientating the crystal for lower energy build up (mixed orientation), using diamond dies which avoid welding of the coating to traditional tungsten carbide dies or in the best case a thermal resistant lubricant.

Wire/Rubber Adhesion

- Nickel does not form Ni_xS_y which was considered to be the mechanical bond for the adhesion system ! at the start of the project. No NiS was ever found at the interface of the several wire/rubber samples examined in this work. In fact pure nickel was shown not to adhere to natural rubber compounds with or without a cobalt salt addition.
- Interface analysis showed no tangible interface products hence it is considered that bonding is related to a chemical bond between zinc in the coating and sulphur in the compound. To bond, a cobalt salt is required in the rubber compound. Zinc crystals in the plating is covered with a thin oxide film of zinc oxide and we hypothesise that the cobalt acts to remove this film chemically so that the pure zinc can bond with the sulphur in the rubber compound.
- The corrosion resistance of the ZnCo coating is 50 times superior to brass and 2 times superior to zinc. The latter is due to enrichment of the 'coating at the iron interface with cobalt due to the phenomena of "anomalous" plating.
- Adhesion degradation of the coating occurs by the formation of ZnS and/or ZnO. Green ageing degradation is due to the formation of zinc carbonate. The above is the current state-of-the-art in this field and constitutes a major scientific advancement.

Acknowledgements

The partners wish to acknowledge the financial and managerial support of the EC for this project BREU-0424.

References

1. G. Orjela" A New Wire/Rubber Adhesion System for Tyres" Tyre Technology 1994, p70

2. G. Orjela, M. Cipparrone, F Pavan, PJ Boden and F Tommasini" A New Wire/Rubber Adhesion System for Tyres - Part 1. Plating Technology" Paper at The Wire and Cables Congress in Florence Italy, Oct 5/6 1995.

3. H Yan, J Dowries, SJ Harris and PJ Boden, "Morphology and fine structure of zinc electrodeposits", Phil. Msg. A, 1994, 70 (2), 391-404.

4. H Yan, J Dowries, SJ Harris and PJ Boden, "Zn-Co electrodeposits: heterogeneous structure and anomalous deposition", Phil. Msg. A, 1994,70 (2), 373-489.

5, H Yan, J Dowries, PJ Boden and SJ Harris "Laminated structure and anomalous deposition of Zn-Co electrodeposits", Proc. Second Symposium of Deposited Thin Films, ed. M Paunovic, The Electrochemical Society, Vol 94-31, 1995,229-240.

6. H Yan, J Dowries, PJ Boden and SJ Harris "A model for nano-laminated growth patterns in Zn and Zn-Co electrodeposits", J. Electrochem. Sot., in press

7. SJ Harris, Feng-bin Li, IR McColl and PJ Boden, " Early stages of Zn-Co electrodeposition imaged by Atomic Force Microscopy", 188th Meeting of the Electrochemical Society, Chicago, 1995, Paper 351.

8. H Yan, J Yu, PJ Boden and SJ Harris, " Mechanisms of anomalous deposition of zinc-iron group alloys", 188th Meeting of the Electrochemical Society, Chicago, 1995, Paper 364.

9. Patent Application: 24/2/94 - M194 A 000335 for new coating by Pirelli